

# Defect-induced ferromagnetism in fullerenes

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## Abstract

Based on the *ab initio* electronic structure calculations the picture of ferromagnetism in polymerized  $C_{60}$  is proposed which seems to explain the whole set of controversial experimental data. We have demonstrated that, in contrast with cubic fullerene, in rhombohedral  $C_{60}$  the segregation of iron atoms is energetically unfavorable which is a strong argument in favor of intrinsic character of carbon ferromagnetism which can be caused by vacancies with unpaired magnetic electrons. It is shown that: (i) energy formation of the vacancies in the rhombohedral phase of  $C_{60}$  is essentially smaller than in the cubic phase, (ii) there is a strong ferromagnetic exchange interactions between carbon cages containing the vacancies, (iii) presence of iron impurities can diminish essentially the formation energy of intrinsic defects, and (iv) the fusion of the magnetic single vacancies into nonmagnetic bivacancies is energetically favorable. The latter can explain a fragility of the ferromagnetism.

## 1 Introduction

Carbon plays unique role in nature, from nucleosynthesis processes in stars to its crucial importance as a basic material substrate of life. It is not surprising therefore that all its properties is a subject of great interest. Magnetic properties of elemental carbon were studied in a context of geology and cosmology [1], biochemistry [2], physics [3], and material sciences [4]. The possibility of intrinsic long-range magnetic order in carbon is intriguing from both basic and applied scientific point of view since the properties of *sp*-electron magnetic materials can be essentially different from conventional itinerant-electron ferromagnets, in particular, it follows from general theoretical considerations that they may be perspective candidates to magnetic semiconductors with the Curie points  $T_C$  above room temperature [5].

The first observation [6] the ferromagnetism with  $T_C$  about 500K in polymerized fullerenes attracts much of attention and now this is the most studied magnetic carbon-based system. The experimental data are still very controversial and there is still no common opinion about intrinsic or extrinsic character of this ferromagnetism. The reported results were independently reproduced afterwards [7, 8] and conditions of appearance of the ferromagnetism in polymerized fullerenes were studied in more detail [7, 9, 11, 12, 13, 10]. It was found that the ferromagnetism arises only in a very narrow range of pressure and temperature in the vicinity of the point where fullerene cages are collapsed [7, 13] (for a general review of current status of the problem, see Ref. [14]). A typical criticism [14] which always occurs when discussing ferromagnetism in *sp*-electron systems with small magnetization (cf. the discussion for  $CaB_6$  [5]) is a possible contamination of samples by iron and iron-based compounds due to use of metallic tools, however, a very careful experimental procedure avoiding this problem is described in Ref. [13]. The most serious criticism that have even resulted in the retraction of the first report [16] was presented in Ref. [15] where on the base of closeness of the Curie temperatures of ferromagnetic  $C_{60}$  and cementite ( $Fe_3C$ ) the effect was attributed to the presence of the latter phase. An idea of crucial role of Fe impurities and formation of ferromagnetic  $Fe_3C$  phase can not explain the disappearance of ferromagnetism beyond a very narrow pressure and temperature interval of sample preparation [7, 8, 13] since under high temperatures and pressures the cementite decays into kish graphite and pure iron, the latter having even higher Curie temperature than cementite. Also, it is very difficult to explain in these terms a strong dependence of the magnetization of photopolymerized fullerenes on the choice of oxygen-free or oxygen-rich formation conditions [11]. The Curie temperature about 820K which was observed in one of the samples [8] does not coincide with those for cementite and  $\alpha$ -iron. It is important to stress that, actually, only magnetic carbon systems synthesized from ethanol [17] can be considered as pure enough in a sense of iron impurities whereas natural materials such as coal and graphite always contain noticeable amount of iron and cannot be completely purified [19, 20, 21]. Thus, nanotubes prepared from them are also contaminated by iron [22] and iron oxides [23] which are rather difficult to eliminate [24]. It is not surprising therefore that sometimes an amount of iron in fullerene samples under discussion is as high as  $400\mu\text{gr}/\text{gr}$  [6, 25] but sometimes it is negligible [13]. However, for the clearest samples in Ref.[13] ferromagnetism was not observed so, indeed, it is a temptation to connect the ferromagnetism of polymerized fullerenes simply with some iron-based magnetic phases, such as elemental iron, magnetite  $Fe_3O_4$ , or cementite  $Fe_3C$  [15]. However, this cannot explain the whole set of experimental data

available. First, magnetic characteristics of all these phases are well known and usually do not coincide with those of the “magnetic carbon” [10], besides that, X-ray emission spectra of carbon in cementite are rather peculiar which allows us always to distinguish cementite from other carbon compounds [26]. The magnetic measurements was used already to separate intrinsic carbon magnetism from that of “parasitic” phases [1] (for polymerized fullerenes it was done in Ref. [10]). Also, even intentional introduction of iron to carbon systems is not sufficient to produce the ferromagnetism [27, 28].

In last few years new results appear about ferromagnetism in heavy-ion irradiated fullerene films [29, 30] and proton irradiated graphite [31]. The x-ray magnetic circular dichroism measurements demonstrate magnetic moments on carbon in proton irradiated graphite [32]. Another argument for intrinsic character of carbon magnetism were discussed in Ref. [33] based on experimental data on  $C_{60}H_{24}$ . This provides some additional arguments in favor of possibility of intrinsic carbon ferromagnetism under certain conditions. To summarize the experimental data discussed above, one can conclude that there is a correlation between contamination by iron and ferromagnetism in the polymerized fullerenes [14] but it cannot be probably explained by the most straightforward way, as a result of formation of iron-based ferromagnetic phases. At least, some experimental data seem to be in disagreement with this view. Actually, the role of iron impurities in the problem of magnetic carbon may be more subtle and some more complicated opportunities can be considered, e.g., a formation of different molecular magnets based on charged fullerenes, with the Curie temperature  $T_C$  above room temperature (see Ref.[34] and references therein). In principle, this might explain a variety of  $T_C$  values in magnetic fullerenes as well as a fragility of their ferromagnetism. However, these systems [34] are periodic crystals and it is not known whether they can be ferromagnetic, with high enough  $T_C$ , under the disorder, or not. Also, they have specific Raman spectra different from those observed in the magnetic fullerenes.

Another possible explanation is a catalytic activity of transition metals, in particular, iron, and their oxides, which are usually exploited for the nanotube growth [35, 36, 37]. One can assume that iron impurities can initiate a formation of various defects responsible for the ferromagnetism. It is the scenario which will be discussed further.

Thus, the nature of magnetism in carbon based systems is still an open issue and thus theoretical investigations can be very useful. Based on first-principle calculations of electron energy spectra and comparison with relevant experimental data it was shown [38] that the ferromagnetism cannot be an intrinsic property of ideal rhombohedral crystal lattice of the polymerized fullerenes. A role of doping by light elements in the appearance of ferromagnetism has been studied theoretically in Ref. [40]. A possible relation between vacancies and magnetism in carbon based systems was investigated intensively in last years. It is known [44, 45, 46] that a single vacancy in graphene produces a local magnetic moment about  $1.2 \mu_B$ . At the same time, the vacancies in fullerenes were studied rather in a context of their role in structure stability of carbon cages [41, 42] and information about their magnetic properties is rather poor. Magnetic interactions between vacancies in the polymerized fullerenes were studied in Ref. [43] but only for a one special kind of vacancies. The model proposed in Ref. [43] cannot explain the ferromagnetism of proton-irradiated samples [29, 30], as well as conservation of ferromagnetism after the depolymerization [11]. At the same time, keeping in mind strong suspicions about an extrinsic character of “carbon” magnetism a theoretical clarification of issues on iron-carbon phases and metal impurities is necessary which was not done yet.

Here we present the results of first principles calculations of magnetic and structural properties of various types of vacancies in fullerenes. It turns out that the recombination of magnetic single vacancies into non-magnetic bivacancies (which have the lower energy than a pair of the single vacancies) is the main limiting factor. This probably explains appearance of the ferromagnetism only in a narrow interval of pressure and temperature [13] which was not discussed in the earlier theoretical considerations. Based on our computational results we present also some arguments against decisive role of iron confirming that the ferromagnetism can be an intrinsic property of (defected) carbon systems.

## 2 Computational method

We used the SIESTA package for electronic structure calculations [47, 48] with the generalized gradient approximation for the density functional [49] with energy cutoff 400 Ry, and  $k$ -point  $8 \times 8 \times 8$  mesh in Monkhorst-Park scheme [50]. Coordinates of atoms and lattice parameters were taken for perfect (defect-free) cubic  $C_{60}$  structure from Ref. [51], and for perfect tetragonal and rhombohedral phases from Ref. [52]. Calculated electronic structure for both cubic and rhombohedral  $C_{60}$  are in a good agreement with the experimental X-Ray spectra [38].

### 3 Iron impurities on C<sub>60</sub>

First, we investigated possible segregation of Fe impurities. To this aim, we have calculated solution (defect formation) energy for two Fe atoms situated in the same C<sub>60</sub> ball and its dependence on the distance between impurity for both cubic and rhombohedral phase, with the optimization of atomic positions in the buckyball. The lattice constants were kept fixed as it should be in the case of small impurity concentration. The defect formation energy was calculated as  $E_{form} = E_{C_{60}+nFe} - E_{C_{60}} + nE_{Fe}$ , where  $E_{C_{60}+nFe}$  is the energy of the ball C<sub>60</sub> with adsorbed  $n$  atoms of iron,  $E_{C_{60}}$  is the total energy of pure C<sub>60</sub>, and  $E_{Fe}$  is the total energy of  $\alpha$ -Fe per atom. Different geometric configurations for these calculations and the calculated energies are shown in Fig. 1. It is seen that for the cubic phase the single Fe atom per C<sub>60</sub> ball has the highest energy whereas for the pair of atoms the energy decreases with the distance decrease. This means that iron impurities in the cubic phase will segregate, indeed. However, for the rhombohedral phase the tendency is opposite. The formation energy in this case is the lowest for the single atom at the apex of the buckyball and for the pairs of Fe atoms it *decreases* with the distance increase. For the atomic configuration shown in Fig. 1g the formation energy is smaller than for the single atom which is probably related with geometric distortions of the C<sub>60</sub> sphere, the iron atom being located in the void between neighboring buckyballs. We have calculated additionally the formation energy for the single Fe atom situated near the central part of rhombohedral carbon cage (Fig. 1i). This corresponds to the minimal energy. Thus, for the rhombohedral C<sub>60</sub> the segregation of Fe looks energetically unfavorable. Instead, at high concentration of impurities one can expect a formation of linear chains metal-buckyball-metal... which were experimentally observed for the mixture of cobalt with C<sub>60</sub> [39].

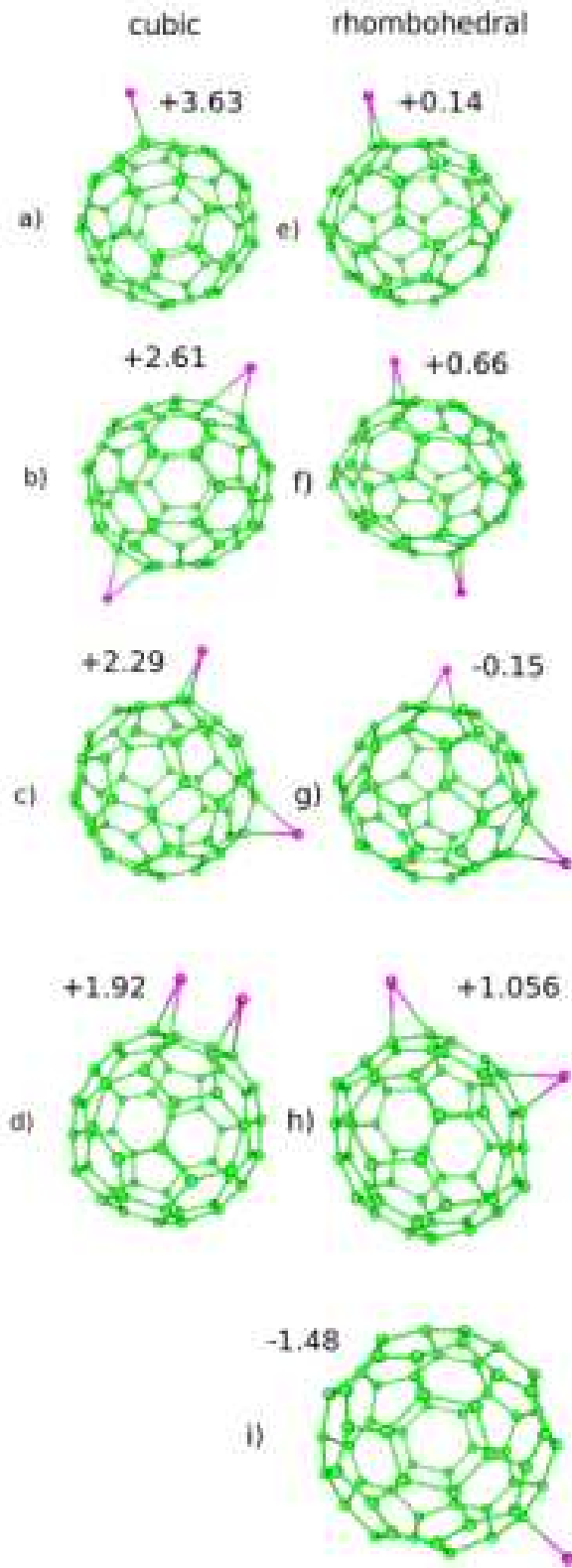
### 4 Vacancies in C<sub>60</sub>

The vacancy formation energy was calculated as  $E_{form} = E_{vac} - E_{C_{60}}(60-n)/60$ , where  $E_{vac}$  is the total energy of the system with single vacancy per buckyball. As was shown in Ref. [43] the vacancies can be responsible for ferromagnetism of fullerenes. The main problem is their too high energy formation, at least, in the cubic phase [41]. However, the vacancy energy is sensitive to local geometric structure of fullerenes and, as we will show, there is an essential difference between cubic and rhombohedral phases. Figure 2 shows a pictorial view of the cubic, tetragonal and rhombohedral phases. Whereas all atoms in the cubic phase are equivalent, already in the tetragonal one there are several different types of vacancy positions, due to formation of covalent bonds between the buckyballs and their distortions. We have performed calculations of the vacancy formation energy removing nonequivalent single atoms as shown in Figure 2. The calculated formation energy for the cubic phase is 5.58 eV which is smaller than the value 7.2 eV for graphene [54]. In the tetragonal phase there are three types of the vacancy positions, the formation energy being decreased from the apex of the buckyball to its center. This is a consequence of the carbon-carbon bonds between the buckyballs in the central area which leads also to partial suppression of magnetic moments of these vacancies. The calculated formation energies for the tetragonal phase vary from 4.67 eV to 6.28 eV. Similar to Ref.[43] magnetic moments on vacancies are strongly dependent on geometric structure of fullerene.

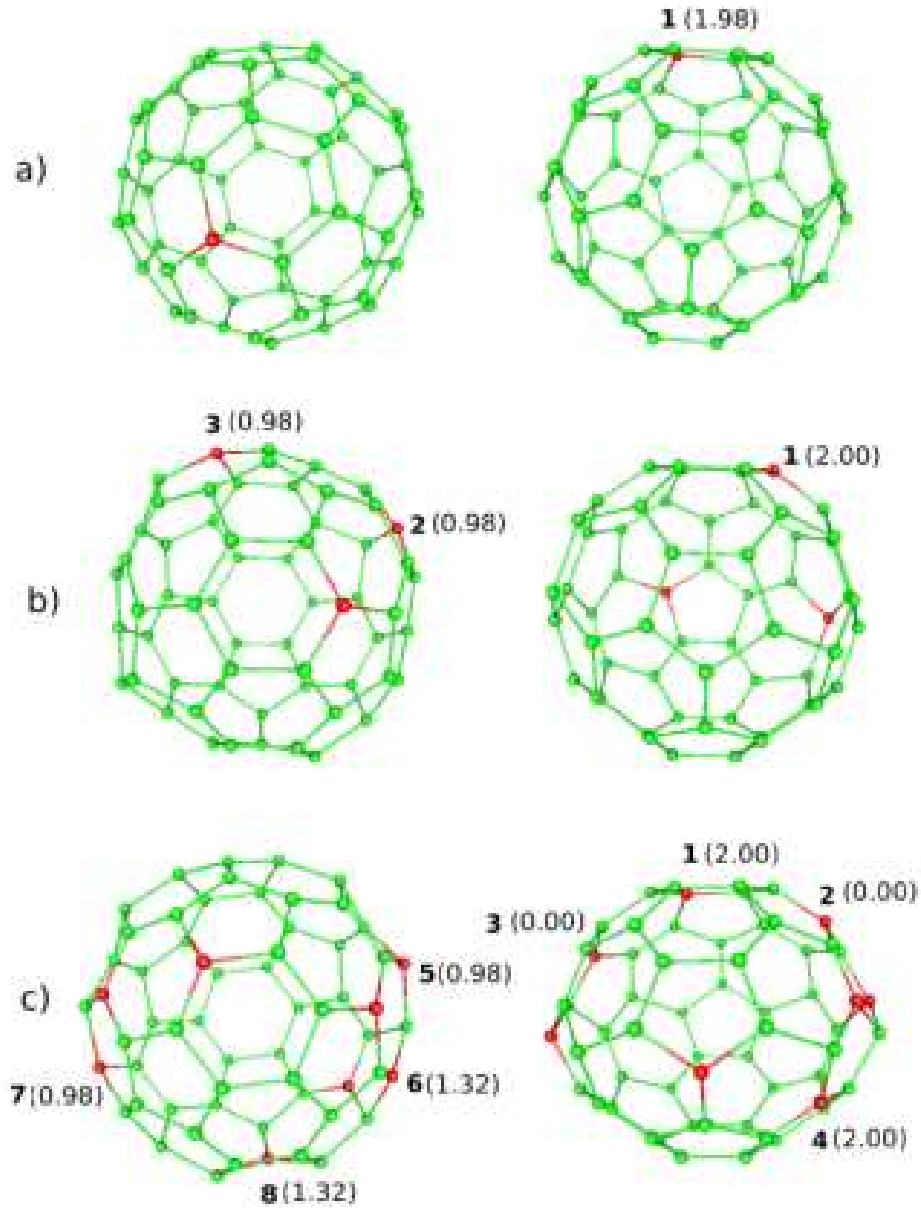
The rhombohedral C<sub>60</sub> is characterized by a larger number of the C-C bonds and, as a result of polymerization, the ball is compressed by 8.4% along  $Z$  axis and expanded in the perpendicular directions and, thus, essentially different parts can be separated, the central one and two “capping” parts. The formation energy for vacancies in the capping parts (atoms 1 - 4 in Figure 2c) is about 5 eV which is close to corresponding values for other C<sub>60</sub> phases. However, for the central part (atoms 5 - 8 Figure 2c) the vacancy formation energy is much smaller and for the atoms 5 and 7 it reaches 3.22 eV. That is why, probably, the polymerization at high pressure and high temperature is the way to magnetic carbon: it diminishes the vacancy formation energy and thus leads to a drastic increase in the vacancy concentration.

The magnetism on the vacancies turns out to be rather fragile. The broken bonds required for magnetism are, at the same time, active centers for chemisorption. As a result, the magnetic moments can be destroyed by impurities. We have calculated the energy of oxygen chemisorption on a single vacancy. It is equal to -1.114 eV for the most energetically favorable vacancy in the rhombohedral case. At the same time, for the vacancy in cubic phase this energy is *positive* and equals 0.716 eV. These data can explain suppression of ferromagnetism at the photopolymerization of C<sub>60</sub> under oxygen-rich conditions [11].

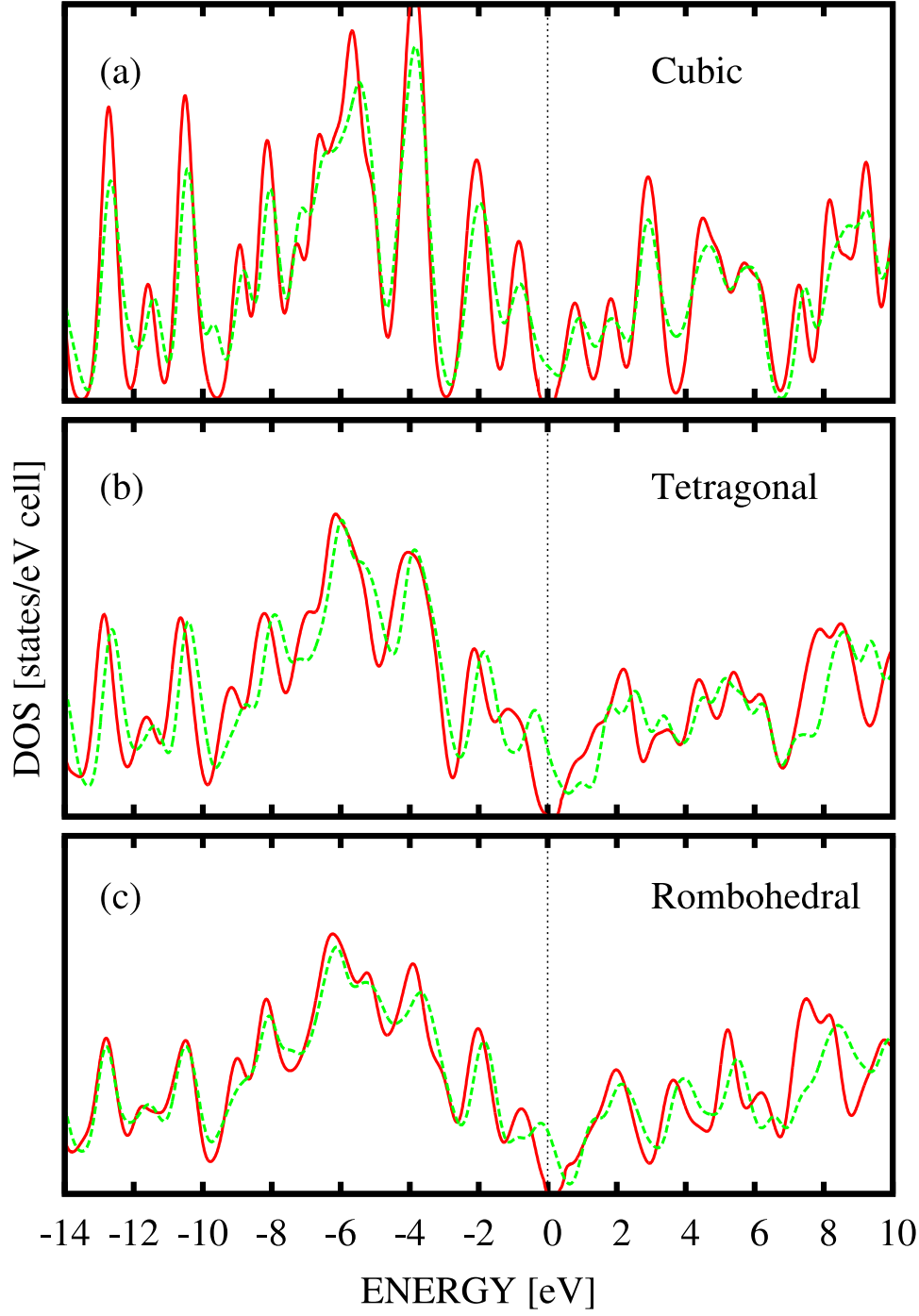
Figure 3 presents electron densities of states for all studied phases of C<sub>60</sub> with and without vacancies. At a large energy scale, vacancies modify the electronic structure rather weakly so it would be difficult to see their effects in, say, X-ray spectra [38]. At the same time, they change essentially the electronic structure in the close vicinity of the Fermi level producing conduction electrons in the former energy gap. Note that experimentally



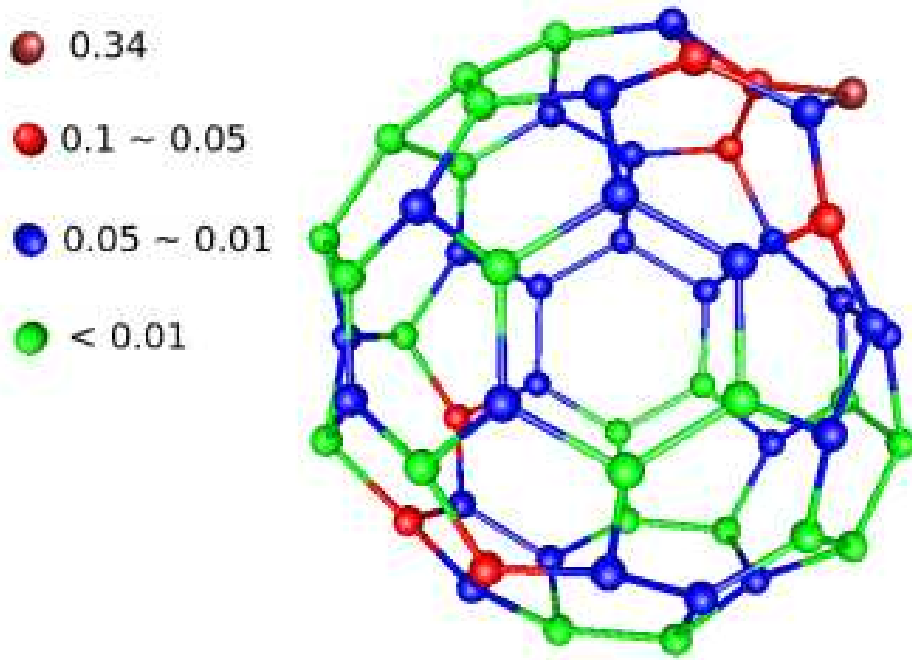
**Figure 1:** Optimized geometrical structure of iron atoms adsorbed on  $C_{60}$  in cubic and rhombohedral phases. Numbers near the pictures are defect formation energies per iron atom, in eV.



**Figure 2:** Top (left) and side (right) view of cubic (a), tetragonal (b) and rhombohedral (c) fullerenes. Red (dark) spheres show inequivalent atoms which can be removed. The values of magnetic moments per whole buckyball are shown in parentheses (in  $\mu_B$ ).



**Figure 3:** Total densities of states for (a) cubic, (b) tetragonal, (c) rhombohedral fullerenes. Solid red and dashed green lines correspond to the system without and with vacancy, respectively.



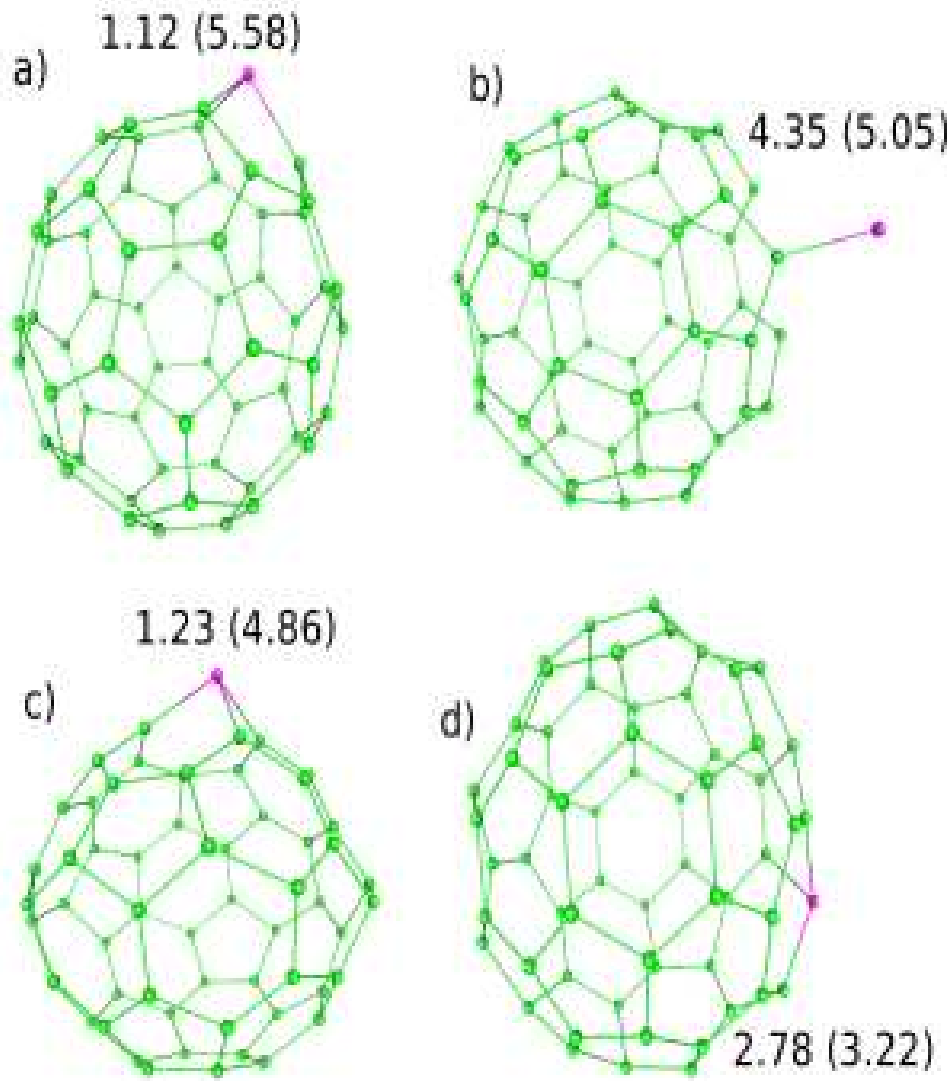
**Figure 4:** Distribution of magnetic moments in  $\mu_B$  on  $C_{60}$  sphere with single vacancy in rhombohedral phase.

magnetic samples turned out to be conducting [12]. These charge carriers may be responsible for ferromagnetism appearance in a narrow defect band [5].

To estimate the exchange interaction energy responsible for possible magnetic ordering we have performed a total energy calculation for a supercell containing two  $C_{60}$  balls with single vacancy per ball, with parallel (FM) and antiparallel (AFM) spin orientations. The calculations have been done for both cubic and rhombohedral phase, in the latest case the vacancies with the lowest formation energy being considered. For both systems the atomic relaxation has been taken into account. We have found that the difference between total energy in FM and AFM configurations is 0.41 eV for the rhombohedral phase and 0.53 eV for the cubic one. These values are close to those calculated for the hydrogen-doped  $C_{60}$  [40]. This energy difference is very high which can be explained by a peculiar distribution of the electron spin density. Whereas in open structures like graphene the magnetic moments from vacancies and impurities are rather localized, with a fast decay of the spin density [53, 46], in closed structures such as  $C_{60}$  the magnetic moments distribute over the whole buckyball (see Figure 4, cf. Ref. [40] for the hydrogen-doped fullerenes). Of course, the value of exchange interactions between distant balls with the vacancies will be weaker than that between the neighboring ones so our calculation gives just an upper limit for the value of magnetic interactions. Various concentration of fullerenes with vacancies will result in various distances between them and, thus, with various exchange parameters and Curie temperatures which seems to be in agreement with experimental data showing a large variance of  $T_C$  in polymerized fullerenes, from 550 K to 800 K.

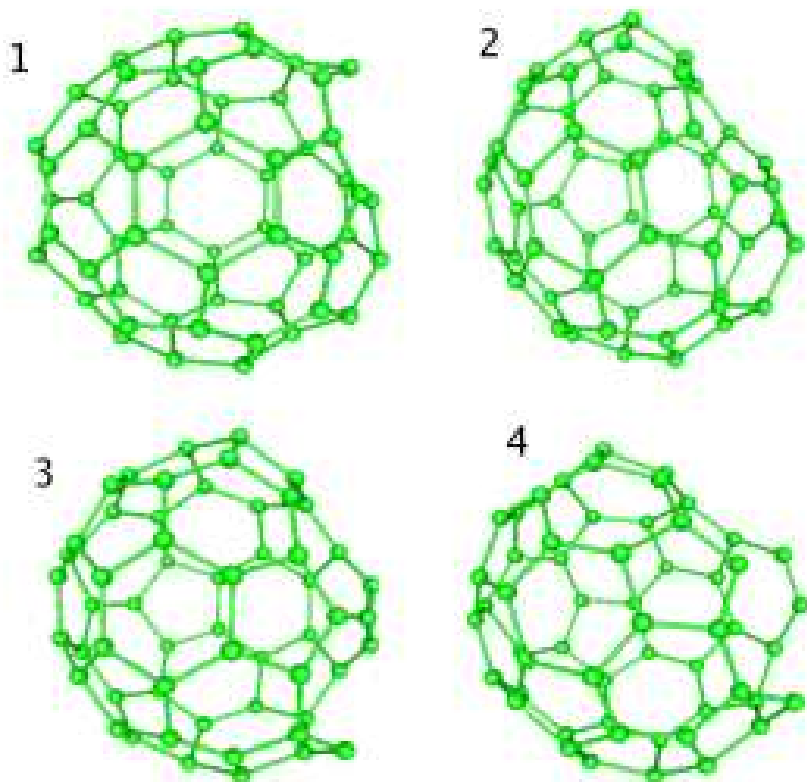
Let us consider now an effect of iron impurities on the vacancy formation in fullerenes. By analogy with the process of ripping of few layer graphene by iron nanoparticles [55] the formation energy will be calculated by the expression  $E_{form} = E_{C_{60}Fe} - E_{C_{59}Fe} - E_{C_{60}}59/60$ . As the simplest model we consider the system  $C_{60}Fe$  where carbon atom closest to the iron impurity is removed. We start with the cubic phase of fullerene. The computational results are presented in Fig.5a. One can see that in the presence of Fe the vacancy formation energy is drastically decreased. Since the iron atoms in cubic phase tend to segregate as was discussed above this calculation deals with rather hypothetical situation than real one. However, a similar tendency holds also for the polymerized fullerenes. As shown in Fig.5b-d for all positions of Fe under consideration the vacancy formation energy is essentially lower than without iron. Because single iron atoms without magnetic carbon impurities in neighbors stay paramagnetic centers [28]. Thus, contamination by iron can initiate a formation of defects responsible for ferromagnetism. The effect of Fe on the vacancy formation considered here may be also interesting in light of simulation of metal-fullerene systems for potential application in hydrogen storage [57, 56].

Based on the computational results one can conclude that vacancies can be a cause for the ferromagnetism

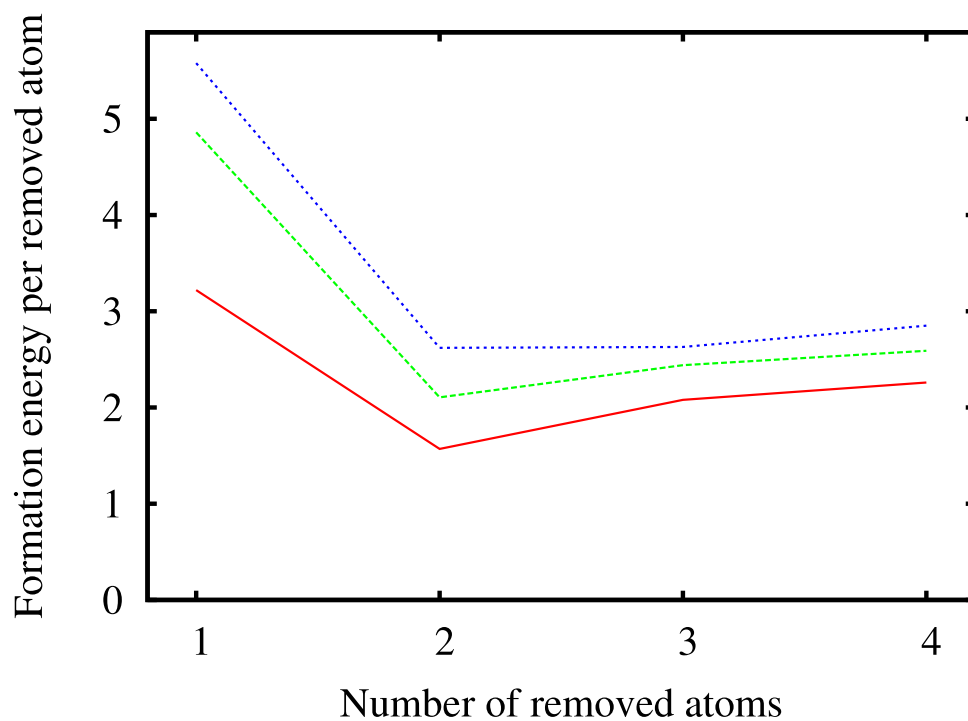


**Figure 5:** Optimized structures of fullerenes with iron impurity and carbon vacancy nearby for cubic phase (a) and nonequivalent positions in rhombohedral (b)-(d). The numbers correspond to formation energies of the vacancy in electronvolts with (without) Fe impurity.





**Figure 6:** Optimized geometrical structures of mono-, bi-, tri- and quadrovacancies in rhombohedral  $C_{60}$ .



**Figure 7:** Energy formation for multivacancies per removed atom as a function of the number of removed atoms in central part of rhombohedral  $C_{60}$  (solid red line), on top of the rhombohedral  $C_{60}$  (dashed green line), and in cubic  $C_{60}$  (dotted blue line).

of polymerized fullerenes. To understand, in a framework of this picture, why the ferromagnetism is so fragile and why it disappears at the temperature of pressure increase the energetics of multivacancy formation has been considered. We have calculated the energies and magnetic moments for bi-, tri- and quadrovacancies for both cubic and rhombohedral  $C_{60}$  (see Fig. 6). The computational results presented in Fig. 7 demonstrate that the formation energies per removed atom for the bivacancies are smaller than for the single vacancy, similar to the previous results for graphene [54]. Therefore, the process of vacancy fusion into the bivacancy is energetically profitable. The bivacancy is always nonmagnetic since there is no unpaired electrons in the situation of *two* broken bonds. This explains a very narrow temperature and pressure interval where the ferromagnetism in polymerised  $C_{60}$  arises: further increase of the pressure or temperature stimulates the process of the bivacancy formation. Figure 7 shows that the appearance of the multivacancies is the most probable in the central part of rhombohedral  $C_{60}$ . This is exactly the place where the cage collapse happens as is confirmed by observation of curved fragments of fullerenes in the “hard carbon” after the cage collapse [58, 59].

## 5 Conclusion

Thus, the explanation of appearance and disappearance of ferromagnetism in polymerized fullerenes in terms of vacancies seems to be consistent with the whole set of experimental data. According to this picture, the ferromagnetism arises under rather restrictive conditions where the monovacancies are formed but their fusion into nonmagnetic bivacancies can be prevented. Oxygen chemisorption will also suppress the ferromagnetism due to formation of chemical bonds involving unpaired electrons associated with the vacancies. We have discussed also mechanisms of the cage collapse via formation of quadrovacancy in the central part of buckyballs. We have demonstrated that a segregation of iron impurities in the rhombohedral fullerene is energetically unprofitable, in contrast with the cubic one. Importantly, a contamination by iron can decrease the vacancy formation energy in fullerenes.

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